

TRANS FREE HARD STRUCTURAL FAT FOR MARGARINE BLEND AND SPREADS

Description

We hereby declare the invention for which we pray that a patent be granted for the product and the process by which it is performed which is particularly described by the following statements: -

The present invention is concerned with a Trans free hard structural fat suitable for the manufacture of low SAFA (Saturated Fatty Acid) poly/mono unsaturated margarine and spreads and fat blends for margarine/spreads using the above mentioned structural fat. This structural fat is made from selectively fractionated non-hydrogenated palm oil fraction, which is interesterified with dry fractionated non-hydrogenated palm kernel fraction to obtain hard structural fat with high yield ratios that can be economically and commercially used as structural fat for the manufacture of Trans free low SAFA, poly unsaturated/mono unsaturated margarine/spreads.

Historically emulsified fat system in margarine/spreads has been designed to satisfy customer requirements such as significant cooling impact, a rapid sharp melt sensation, and no coated or waxy feel on the tongue. In addition, it should impart temperature cycling stability (heat stability) as well as spreadability when taken out frequently from the refrigerators are the prominent features.

To achieve these objectives, margarine fat blend is being formulated using hard stocks derived by hydrogenation of liquid oils.

However, with the adverse effect of Trans fatty acids being published, consumers are looking for margarine/spreads with practically no Trans fatty acids.

This can be achieved by using fully hydrogenated fats as structural fat, which usually does not contain Trans fatty acid or very negligible amount.

Hydrogenation process is generally viewed as the main reason for the development of Trans fatty acids in oils and fats. Hence, there is a strong consumer perception against usage of and hydrogenated oil/fat in the food products including margarine/spreads.

Hence research work is being carried out for development margarine/spreads using no hydrogenated oils in their hard stock at the same time looking at the possibility of reducing the saturated fatty acid levels (SAFA) in the products.

For the purposes in understanding, the terms 'oil' and 'fat' are used synonymously in the present disclosure.

Theoretical Considerations

The hard stock contributes triglycerides especially of the trisaturated type. A certain minimum quantity of these is essential to provide the "structural fat" and to prevent oiling out of the liquid oil. From the patent literature and general experience, this minimum quantity is around 6%. More is acceptable and desirable if the amount of H_3 , being tri-glycerides with 3 carbon chain of length C16 carbon chain residue and above that are saturated, and especially tristearin, is not greater than 2% otherwise poor mouth feel will result. Hence content H_2M , being triglycerides which have 2 carbon chain length that are C16 and above and saturated and one chain of carbon length C14 and below, is valuable, to give the structuring effect, hence the need for a lauric oil.

When the hard stock components are interesterified, the amounts of trisaturated triglycerides in the interestified product are determined entirely by the content of saturated fatty acids (saturated FA) in the blend. This relationship is very critical as shown by the results:

% Saturated FA in the Oil blend	% Trisaturated Triglycerides After Interesterification
50	13
60	22
70	34
80	51
90	73

Taking sunflower oil as the PUFA (polyunsaturated acids) oil to be used in the blend, at a level of 80% (SAFA 10.3%) then the hard stock should not contribute more than 11.76% SAFA to the final blend considering that the SAFA content of polyunsaturated margarine should not exceed 20%. If 20% of the hard stock were used for the margarine blend along with the Sunflower oil as above (a high usage level) – and if we also want a minimum of 6% trisaturated Tgs (triglyceride) in the final blend, it can be seen from the above table that the SAFA content of the hard stock must be about 67% so that interesterified hard stock has 30% trisaturated triglyceride. Assuming only 15% hard stock is used then the SAFA content of the hard stock must be about 74%, so that it has 40% trisaturated triglyceride after interesterification. These are minimum requirements and higher amount of trisaturated Tgs would be desirable.

The usage of hard structural fat in the blend can be 5 to 25% and the liquid oil of its blends can be 95 – 75%.

The following abbreviations are set out below, for the purposes of the ease of understanding the terms as used in the description and claims. It is understood that these terms are terms used commonly in the art in that:

FA = fatty acid, PUFA = poly-unsaturated acid(s), SAFA = saturated fatty acid(s), MUFA= Mono unsaturated Fatty Acids, H = saturated FAs with carbon numbers greater than or equal to 16, M = saturated FAs with carbon numbers less than or equal to or less than 14.

C = refers to carbon chain number. The term "carbon chain residue", "fatty acid residue", "carbon chain number" as well as "carbon chain length" etc used in the present patent specifications are synonyms. The term "hard stock" refers to the structural fat.

H₃ refers to triglycerides with 3-carbon chain of length C16 carbon chain residue and above that are saturated.

H₂M refers to triglycerides which has 2 carbon chain length that are C16 and above and saturated and one chain of carbon length C 14 and below. Tg's refer to triglyceride.

Further, the solid fat content (SFC) in this description and claims is expressed, as N-value using nuclear magnetic resonance method. The method used is IUPAC method 2.323. The fat is heated to a temperature of 80 °C and filtered and filled in SFC tubes. The temperature is maintained at 60° for at least 5 minutes, keeping the sample for 1 hour at 0 °C, and then 30 minutes at the measuring temperature. The SFC values are measured using Bruker Minispec-120 instrument.

The term "liquid oil" is used in this invention refers to glyceride mixtures that are pourable at 5 °C. Preferably the solid fat content of the liquid oil is 0 at 20 °C

"Fractionation" is a process used for separation of high melting component from a feed stock, The higher melting solid fraction obtained is called as "stearin" fraction or a "hard" fraction and lower melting liquid fraction is called "olein" fraction. Throughout this specifications, the term 'stearin fraction' as well as term 'olein fraction' means higher melting fraction and lower melting fraction respectively.

The interesterification process is a well-known art and a more recent review of the same is published by Rozendaal & Macrae (1997). When the interesterification process is carried out using alkali metal catalyst (0.1-0.2% sodium methoxide catalyst (sodium methylate (NaOCH₃)-UN No.143) also known as Natrium Methylate is used as catalyst), it leads to a random distribution of triglycerides in which the fatty acids are distributed randomly over the 1-2-and 3-position of the glycerol moiety. The number of tri-glycerides produced by interesterifying a fatty mixture containing n fatty acids is: $\frac{1}{2}(n^2+n^3)$. This interesterification process is generally termed as a random chemical interesterification. The interesterification process used in this invention is based on this process

The manufacture of margarine and spreads are known in the art, and described in various text books, for e.g. The Chemistry and Technology of Edible Oils and Fats and their High Fat Products by G. Hoffmann; Academic Press London 1989, page 319 ff and in particular page 320-321.

Carbon chain number analysis is a well-known technique in the art. A suitable description is given in EP 78,568.

In this specification, all parts, proportions and percentages are by weight. The amount of fatty acids in an oil or fat is based on the total amount of fatty acids in said oil or fat and the amount of hard fraction or hard fat in the fat composition is based on the total weight of said fat composition, unless otherwise stated.

Prior Art

For manufacturing Margarine/Spreads, the fat blend should be such that it has a flat melt profile from 5 to 30 Deg C at the same time low solids at 35 and 40 deg C so that the product has good mouth feel. The blend should be such that the product does not oil out and has good temperature cycling stability.

Further, in recent years due to high publicity in the media with respect to adverse effect of Saturated as well as trans fatty acids, many manufacturers have taken nutritional approach to manufacture the product by reducing the saturated as well as trans fatty acids and increasing poly /mono unsaturated fatty acids in the margarine/spreads as well as shortening.

Margarine/Spreads have, been on the market for some time aiming to meet this need. Typically, the margarine fat of these products consists of about 87% liquid oil, e.g. sunflower oil and 13% of a hard stock consisting of a random interesterified mixture of fully hardened lauric fat, e.g. fully hardened palm kernel oil, and fully Hardened palm oil.

Attempts have been made over the years to formulate margarine/spread fat blends by using much lower levels of hard stock. For example EP 89,082 recommended H₂M rich hard stocks. The preferred method described in EP 89,082 for producing such hard stock is randomly interesterifying a partly or fully hydrogenated lauric fat having a melting point [ranging from 30 to 41.degree. C., with a fat, which can be fully or partly hydrogenated, fractionated or non-fractionated, wherein at least 60% of the fatty acid residues are C.sub.16 - or C.sub.18 -fatty acid residues. This C.sub.16 -C.sub.18 fat is preferably selected from palm fat, soybean oil, groundnut oil, sunflower oil, maize oil, and rapeseed oil, having a melting point ranging from 50 to 71.degree. C.; and fractionating the interesterified mixture. Fractionation is preferably done in an organic solvent. The examples of EP 89,082 illustrate spreads comprising margarine fats containing 90 or even 93% sunflower oil and only 7 or 10% hard stock. This hard stock is produced by means of 2-stage fractionation in acetone to obtain a mid fraction of a random interesterified mixture of 50 parts fully hydrogenated palm kernel fat and 50 parts fully hydrogenated. Thus EP 89,082 met the objective of manufacture of Margarine/Spreads with very Low SAFA as well as very PUFA/MUFA by producing a hard Structural fat that can be used at levels as low as 4 %.

However recently consumers have been expressing concern about chemically modifying fats e.g. by hydrogenating or hardening, which result in trans fatty acid residues if partial hardening is involved. Also consumers have been voicing their concern over use of solvent such as Acetone etc as well detergents for fractionation of fats due to possible left over of these chemicals in traces.

Even though full hydrogenation of the oils and fats eliminates the presence of trans fatty acid residues by converting them to saturated fatty acids, still there is a consumer perception that any hydrogenated product is undesirable. Because of this the manufacturers of margarine/Spreads have been looking for alternate hard stock, which do not undergo hydrogenation. Consumers also raise concern over the presence of trace of solvent as well as detergent that may be present in the fat if the same has undergone solvent fractionation /detergent fractionation processes.

To meet the need for spreads with low contents of SAFA in the margarine fat which have been produced without using hydrogenation, CA 2 098 314 proposes to prepare hard stock by chemically interesterifying a blend of generally equal proportions of palm stearin and palm kernel stearin.

However the usage level of such hard stock was 14-21 % especially about 16 % to obtain a good quality product. This high level of usage resulted in higher level of SAFA in the final products. Hence attempts have been made to prepare hard stock that can be used at much reduced levels of even below 14 %.

The comparison of solid fat profile of the hard stock of CA 2098314 with the new invention is given as follows:

CA 2098314		New inventions	
<u>% Solid fat at</u>		<u>% Range of solid fat at</u>	
		<u>Min</u>	<u>Max</u>
10 °C -	64.45	95.0	97.0
20 °C -	49.83	92.5	94.0
25 °C -	45.66	85.2	92.0
30 °C -	34.13	72.5	84.0
35 °C -	22.17	54.3	71.0
40 °C -	10.90	33.7	55.0

It could be seen that the solid fat profile of the product obtained by interesterification of commercially available palm stearin fraction with palm kernel stearin fraction as per CA2098314 produces a low grade structural fat, as it has a very low solid fat profile resulting in high level of usage even at low level at 14%. Compared to this, in the invention, a new process has been developed for dry fractionation of palm/palm stearin fractions and filtration in high pressure membrane filter to obtain a high C16 hard palm fraction with a C16 level of >70% which is used as a component fraction for the interesterification process.

When this hard palm oil fraction with high C16 fatty acid residue was used as a fat blend for interesterification, a structural fat was obtained, which had high solid fat profile so that this could be used at low levels.

This objective was reached to a considerable extent in recent years. For Example in US 5,858,445, US 6,156,370, CA 2207954, as well as in WO 96/19115, the inventors have found that a hard structural fat that can be used at level of 5-14% can be produced without Solvent fractionation, random chemical interesterification as well as hydrogenation process that has been used in EP 89,082. Accordingly, the invention provides a margarine fat blend essentially comprising 86-95% liquid oil and 5-14% of a hard stock, this hard stock being a stearin fraction of an enzymatically interesterified mixture of 25-65%, and preferably 35-55%, unhardened lauric fat stearin and 75-35%, and preferably 65-45%, unhardened C.sub.16+ fat stearin.

By selecting unhardened natural vegetable fat products having sufficient saturated fatty acids, such as lauric fat fractions and palm oil fractions for the enzymatic interesterification, the chemical modification of the fats were reduced to a minimum and the trans fatty acid level in the final fat blend were almost zero.

The hard stock produced from un-hydrogenated fat under US 5,858,445, US 6,156,370, CA 2207954 and WO 96/19115, could achieve quite similar results with respect to the nutritional properties of the spread as in EP 89,082.

However, EP 89,082 focus on fully concentrates on achieving the minimum SAFA content in the product with acceptable product properties and heat cycling stabilities. To meet this requirement, the inventors used all the fat modification techniques including hydrogenation, chemical interesterification, solvent fractionation and even chemical synthesis of triglycerides.

By using Structural fat produced under US 5,858,445, US 6,156,370, CA 2207954 and WO 96/19115 the inventors could substantially match the performance of EP 89,082 without using Hydrogenation, solvent fractionation, and chemical interesterification.

However to achieve this, they had to resort to expensive multi-stage counter current dry fractionation process as per EP 399,597 to produce hard palm C16 fraction. Further, they had to use expensive enzymatic interesterification process for interesterification of Lauric fat as well as Palm fat. Further, the interesterified fat was required to undergo an additional dry fractionation process at 31-41 Deg C to produce hard Structural fat for use in margarine blend. (Solvent fractionation not excluded). This however resulted in very low yield of Structural fat ranging from 14 to 45 %. Since this process produced excessive olein fraction (liquid fraction) as a by-product, alternate use for olein fraction need to be found to get economical value for such fraction. This resulted in the process being commercially un-attractive. Further, inventors used expensive enzymatic interesterification method. To date, the cost of immobilized enzymes required and high capital and variable processing cost involved has made this process un competitive compared to chemical random

interesterification process. This is especially true in case of manufacture of low value products like fats for margarine/spreads/shortening.

Many consumers do not consider enzymatic interesterification as a "truly" natural process as claimed by the inventors. For example, the recent EU Parliament directive No.20000/36/EC of 23rd June 2000 relating to cocoa and chocolate products intended for human consumption, has prohibited use of Vegetable fat which has undergone "enzymatic" fat modification of the triglyceride structure. Further many of the new enzymes are produced by genetic modification and there is again very strong consumer perception against products derived from genetically modified substances (GMO).

We, therefore consider, random chemical interesterification process is more "natural" and a mild process as the alkaline metal catalyst namely sodium methoxide used in the process breaks down as sodium hydroxide. This process is a well-known art in the industry. Sodium hydroxide has been used historically and even to day for the refining of soft oils such as soybean, sunflower, canola etc and such refined oil is consumed widely and even for manufacture of margarine/spreads. Further, chemical interesterification is a well-known art in the industry and needs low level of technology and cost.

We therefore found that this economic and commercial issues involved could be addressed to by inventing new process to manufacture hard palm fraction that could be interesterified with a hard palm kernel fat. We wanted to avoid further fractionation steps of such interesterified fat so that the yield of structural fat is approx 100%. Even if, a further fractionation step was required to produce extra hard structural fat, the focus was how to improve the yield of such hard stock to level of >70 % compared to 14-45 % that were achieved under US 5,858,445, US 6,156,370, CA 2207954 and WO 96/19115.

To this, our approach was to use single or two stages melt crystallization and dry fractionation method to produce a hard palm oil fraction with a C+ 16 level of greater than 70 %, exceeding 83% and total saturated fatty acid level of greater than 90 %. Further our approach was also to use commercially available palm stearin fraction, which is priced much cheaper as compared to palm oil, with a single stage dry fractionation step to obtain hard palm oil fraction. Further our objective was to avoid prior art multi-stage counter current dry fractionation process to achieve such hard palm stearin fraction which is expensive and produced low yield of such fraction.

It is considered essential to achieve maximum level of saturated fatty acids while enriching C-16 type fatty acids in the hard palm oil fraction. If this could be achieved automatically, other saturated fatty acids mainly C-14 as well as C-18 type also get enriched resulting in over all increase of total saturated fatty acids in such hard palm oil fraction to over 90 %. When such fraction is mixed with hard palm kernel stearin fraction with a C-12 level of higher than 52 %, the total saturated fatty acid level in the blend exceeds 90%. Higher level of saturated fatty acids in the blend before interesterification reaction is highly preferred, as this resulted in higher level of

trisaturated triglycerides in the interesterified blend. The reason for this has been explained in detail under the chapter "theoretical considerations".

This goal was achieved in commercial scale operation in the plant by selectively crystallizing the commercially traded palm oil in a two-step fractionation process. In the first step palm oil was fractionated at a lower temperature to produce medium hard palm oil fraction or commercially called palm stearin fraction, by filtering the crystallized slurry through a membrane press. This medium hard palm oil fraction or palm stearin fraction was once again crystallized at a higher temperature to crystallize high melting C-16+ triglycerides and the crystallized slurry was then pumped through a high pressure membrane press to separate the crystals of high C-16 palm oil fraction. After completion of filtration, high squeeze pressure was applied on the membrane (15-35 bar) so as to squeeze out the occluded liquid oil in the hard palm stearin fraction recovered in the filter chamber to enrich the C-16 as well as saturated fatty acids in the hard fraction.

Higher squeezing pressure resulted in increased C-16 level of over 80 %, in the hard fraction and also increased was the total saturated fatty acid level.

It was difficult to obtain such hard palm stearin fraction in the prior art, even by solvent fractionation method as well as expensive multi-stage counter current dry fractionation method. This could be achieved in commercial scale at lower cost by applying high squeeze pressure in the membrane filter to remove the liquid fraction from the hard palm fraction recovered in the filter.

Advantages and problems solved by new invention

It could be seen in the examples given in the prior art process where in the C-16 level in the hard palm fat obtained was only 79.4% and the level of total saturated fat in this fat was only 84.6 %. This was so even by using expensive multi-stage counter current fractionation method. Even usage of solvent fractionation process, which is considered highly selective, yielded a hard palm fraction with a C-16 level of only 77.9 %.

Prior art process therefore used palm fraction, which contained less than 80% C-16 level, even though the claim covered product with higher range. Because of this low C 16 level in the hard palm fraction, prior art process had to embark up on one more fractionation step (including solvent fractionation step) to extract trans free hard structural fat. This additional process resulted in low yield of the hard structural fat and also problem associated with the disposal of olein fraction. Whereas prior art process could only produce 14-45 % hard structural fat, with the new process, it has been in a position to obtain nearly 100 % yield of such trans free hard structural fat, which make the new product as well as process much more economical compared to prior art process.

To achieve high C 16 level concentration in the hard palm oil fraction, the inventor has to work with different chamber depth in the high-pressure membrane press,

finally achieving the desired result when the chamber depth of high-pressure press was reduced below 35 mm and especially better results when the chamber depth was reduced 15 mm and below.

The new hard stock was further separated by conventional panning and pressing to obtain >70 % yield of extra hard structural fat. This pressing was done at a temperature of below 30 deg C. By adoption of this simple process, the inventor could come up with an extra hard structural fat with a very high yield, nearly double to that of prior art processes.

Claims

1. A margarine and spread fat blend comprising 60 – 95% of a liquid oil selected from a group of oils consisting of sunflower oil, Canola oil, soy oil, peanut oil, rice bran oil, olive oil, safflower oil, corn oil or marine oil or the blend of any of the above liquid oils with a Trans free hard structural fat at 40 - 5 % level whereby the said trans free hard structural fat is made from selectively fractionated non-hydrogenated hard palm oil fraction, which is interesterified with lauric fat such as dry fractionated non-hydrogenated palm kernel oil fraction without using hydrogenation process and without using organic solvent or detergent for fractionation and where in
 - a. said hard palm oil fraction is produced. by single or two stage melt crystallization and dry fractionation of palm oil or the stearin fraction thereof, followed by filtration in a high pressure membrane filter where in the membranes of the said membrane filter are inflated at a pressure exceeding 10 bar to recover the said hard palm fraction
 - b. the said hard palm oil fraction having a C-16 carbon chain fatty acid residue level of at least 70%
 - c. the said interesterification process is performed using chemical such as sodium methoxide
2. A margarine and spread fat blend according to claim 1, where the liquid oil blend has high poly/mono unsaturated level such that in the total fat blend the poly/mono unsaturation level exceeds 40%
3. A trans free hard structural fat for use in margarine and spread fat blend according to claim 1 is produced without using hydrogenation process so that Trans fatty acid residue produced during the hydrogenation is eliminated.
4. A hard palm oil fraction for use in trans free hard structural fat according to claim 3 has a C16 carbon chain fatty acid residue greater than 70% and is produced with out using multi stage counter current dry fractionation process, or solvent fractionation process using acetone, hexane or other solvents.
5. A hard palm oil fraction according to claim 4 has a melting point higher than 57 Deg C, and can be flaked as well as converted to powder form for easy handling, because of its high melting point in spite of not being required to undergo hydrogenation and has a solid fat content of > 75% at 40 Deg C
6. A method of producing hard palm oil fraction according to claims 4 and 5, where in palm oil or its stearin fraction is selectively dry fractionated by melt crystallization and single or two stage dry fractionation process and the said hard palm oil fraction is separated in a high pressure membrane filter and the

separated hard palm oil fraction has a C 16 carbon chain fatty acid residue level of >70%

7. A method of producing hard palm oil fraction according to claim 6, which comprises of selectively dry fractionating palm oil or its stearin fraction using a two step melt crystallization process, the first step is being performed between 20-25 Deg C. to obtain a medium hard palm oil fraction by filtration of crystallized slurry through a membrane type filter, and the medium hard palm oil fraction is then once again dry fractionated between 45-55 Deg C, to obtain very hard palm oil fraction with a C-16 carbon chain fatty acid residue of > 70 %, by filtration through a high pressure membrane type filter , the temperature of fractionation being dependent on the iodine number of the medium hard palm oil fraction, obtained in the first fractionation step , the fractionation temperature being dependent up on the type and geometry of the crystallization equipment used and not limited to temperature range specified

8. A method of producing hard palm oil fraction according to claim 6 and 7, which further comprises separating the hard palm oil fraction, in high pressure membrane type filter, wherein a pressure of 10-35 bar is used, to inflate the membrane, so as to remove the liquid fraction occluded in the hard palm oil fraction recovered in the high pressure membrane filter, thus enriching the level of C-16 carbon chain fatty acid residue in it to a level of > 70%,

9. A trans free hard structural fat suitable for use in margarine and spread fat blend according to claim 1,3 wherein the said trans free hard structural fat is produced by interesterification reaction of hard palm oil fraction having a C-16 carbon chain fatty acid residue of > 70% with a hard palm kernel oil fraction, such that the resultant trans free hard structural fat obtained is used as such in the said fat blend with out being subject to further fractionation process

10. A trans free hard structural fat according to claim 9, where in the said trans free hard structural fat is produced by interesterification reaction of hard palm oil fraction with hard palm kernel oil fraction such a way that the said trans free hard structural fat has a trisaturated triglyceride of H₃ type less than 25% wherein H denotes carbon chain fatty acid residue of C 16 and above

11. A method of producing trans free hard structural fat for use in margarine and spread fat blend according to claim 1, comprising of, subjecting a hard palm oil fraction having a C-16 carbon chain residue level of > 70 %, to random chemical interesterification with a hard palm kernel oil fraction having a C-12 fatty acid residue of > 52%, and then subjecting this interesterified fat mixture to a physical separation method of panning and pressing at a temperature of less than 30 deg C so as to recover extra hard trans free structural fat that could be incorporated at a very low levels in the said margarine and spread fat blend.